<Division of Environmental Chemistry> Molecular Materials Chemistry

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- Molecular Materials Chemistry -

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Visitors

Prof HU, Shaohua	Donghua University, China, 1 - 11 July 2004, 18 - 26 October, 2004
Dr AMORNSAKCHAI, Taweechai	Mahidol University, Thailand, 9 - 22 October 2004
Mr CHAIYUT, Nattawut	Mahidol University, Thailand, 1 April - 31 August 2004

Scope of Research

The research activities in this subdivision cover structural studies and molecular motion analyses of highly organized polymer materials in the different states by high-resolution solid-state NMR, electron microscopy, X-ray diffractometry, and so on, in order to develop high-performance and high-functionality polymer materials such as organic electron luminescence devices and different molecular hybrid materials. The structure formation process of bacterial cellulose is also characterized in detail and environmentally friendly cellulosic nanohybrid materials are examined to develop in different stages of the biosynthesis.

Research Activities (Year 2004)

Presentations

Super-High Field Solid-State NMR for Structural Analyses of Advanced Materials, Horii F, 35th Solid-State NMR for Materials Meeting, 11 May (Invited).

Solid-State NMR Investigations of Alq_3 in Different Polymorphs, Kaji H, International Discussion Meeting on Tris(8-hydroxyquinoline)aluminum(III), 22 September (Invited).

Precise Solid-State NMR Analysis of Polymers and Metal Complex Light-Emitting Materials and the Control of their Optical Properties, Kaji H, 45th Symposium on Coordination Chemistry, Jpn., 23 September (Invited).

Solid-State NMR Investigations of facial and meridional Alq_3 in Different Polymorphs, Kaji H, 21COE Workshop on OSE & OEL (Mark Thompson Symposium), 30 October (Invited).

Preparation of Nanocomposites Composed of Highly Crystalline Cellulose Microfibrils and Imogolite, Ikuno M, Hirai A, Horii F, Donkai N, Tsuji M, 53rd Annual Meeting, Soc. Polym. Sci., Jpn., 25 May.

Dynamics of Hole-Transport Material in Organic EL Device, - Analysis of Dynamics by Two-Dimensional Solid-State ^{13}C and ^{2}H NMR Spectroscopy -, Tsukamoto N, Kaji H, Horii F, 53rd Annual Meeting, Soc. Polym. Sci., Jpn., 25 May.

Structure and Structural Change of Sub-elementary Fibrils of Bacterial Cellulose in an Initial Period of Organization, Suzuki F, Tsujitani K, Hirai A, Horii F, 53rd Symposium on Macromolecules, Soc. Polym. Sci., Jpn., 16 September.

Cationic States of a Hole Transport Material in Organic EL Devices, -Analysis by Solid-State ^{15}N, ^{13}C NMR and Quantum Chemical Calculation-, Yamada T, Kaji H, Tsukamoto N, Kusaka Y, Horii F, 53rd Symposium on Macromolecules, Soc. Polym. Sci., Jpn., 15 September.

Grants

Horii F, Precise Solid-State NMR Analyses of Non-crystalline Organized Structure and Dynamics of Polymer Functional Materials, Grant-in-Aid for Scientific Research

A Combined Experimental and Theoretical Study of the Conformation of TPD Using Solid-State ^{15}N NMR and DFT Calculations

The conformation of *N,N'*-diphenyl-*N,N'*-di(*m*-tolyl)benzidine (TPD) (Figure 1), which is widely used as a hole-transport material in organic electroluminescent (OEL) devices, has been studied by solid-state ^{15}N NMR and density functional theory (DFT) calculations [1]. Solid-state NMR is a suitable tool for the analysis of the organic materials in OEL devices, since the materials are normally in the amorphous state and the detailed structures are hard to access by diffraction methods. Figure 1 shows the DFT-calculated ^{15}N NMR chemical shift anisotropy (CSA) spans, $\sigma_{11} - \sigma_{33}$, of amorphous TPD plotted as a function of the torsion angles, α and β. The CSA spans significantly vary depending on the conformation and can be used for the determination of torsion angles. The experimental CSA span of ^{15}N-labeled amorphous TPD was 15 ppm. This corresponds to the narrowest CSA span among the DFT-calculated values in Figure. 1. The DFT-optimized structure with torsion angles α of 40-41° and β of 41-43° gives the narrowest CSA span, indicating that the torsion angles determined by the experimental CSA span agree well with those obtained from the DFT-optimized structure. This confirms that the DFT-optimized TPD single molecule reflects the structure in the condensed amorphous state: the nitrogen atom and the three carbons directly bonded to the nitrogen are in the same plane, and three rings attached to the nitrogen adopt a propeller-shape conformation. Forty stable conformers are considered to exist in the amorphous state. Torsion angles change the shape of molecules and the state of the electron clouds around the nitrogens, and therefore significantly affect the intermolecular electron coupling. It suggests that the torsion angle is a crucial factor for the carrier transport properties.

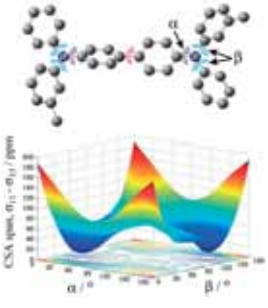

Figure 1. DFT-calculated ^{15}N σ_{11} - σ_{33} values of amorphous TPD as a function of torsion angles α and β.

[1] H. Kaji, T. Yamada, N. Tsukamoto, F. Horii, Chem. Phys. Lett., 401, 246-253 (2005).

Phase Behavior of Aqueous Mixture of Cellulose Microfibrils and Imogolite Nanotubes and Preparation of Their Nanocomposites

Development of functional green polymer materials is a subject of great importance. Phase behavior of the mixture of tunicate cellulose microfibrils and imogolite nanotubes in the aqueous solution of acetic acid (pH=3) has been studied to fabricate cellulose-based nanocomposites. Tunicate cellulose microfibrils prepared by sulfuric acid treatment are rodlike. They are 1-3 μm long and 15-30 nm wide. Purified imogolite nanotubes with an outer diameter of 2.5 nm are estimated at 0.3 μm in length. Both cellulose microfibrils and imogolite nanotubes form their own lyotropic mesophases in the aqueous solution of acetic acid. The imogolite solution separates into the isotropic and liquid crystalline phases above the concentration of 0.8% (A point) in the aqueous solution of acetic acid. In contrast, the microfibril suspension becomes turbid without phase separation at 0.3%, and forms only the liquid crystalline phase above 1.5%. Each mixed suspension of microfibrils/imogolite nanotubes with different weight ratios below 1/1 shows the two phases after one day and the volume of the liquid crystalline phase increases with increasing concentration (Figure 2). Characterization of nanocomposite films prepared from respective liquid crystalline phases of microfibrils/imogolite nanotubes with different weight ratios is in progress.

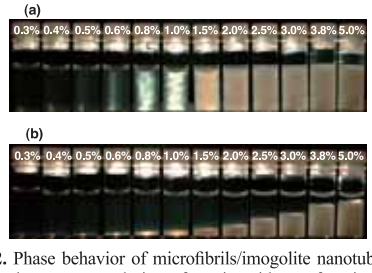

Figure 2. Phase behavior of microfibrils/imogolite nanotubes (1/1) dispersed in the aqueous solution of acetic acid as a function of the total concentration. (a) Immediately after preparation. (b) After 2 months. The turbid phase is the liquid crystalline phase. The concentration of the A point is 0.4%.

(B)(2), 1 April 2004 - 31 April 2006.

Horii F, Hybridization Utilizing Hierarchical Structure of Microbial Cellulose by a Newly Developed Microbiosystem, Grant-in-Aid for Scientific Research, 1 April 2004 - 31 April 2006.

Kaji H, Higher Order Structures and Optical Properties of Light-Emitting Polymeric Materials, PRESTO, Japan Science and Technology Agency, 1 November 2002 - 31 October 2005.

Hirai A, Preparation and Structural Analysis of Bacterial Cellulose/Natural Inorganic Nanocomposites, Grant-in Aid for Scientific Research (C)(2), 1 April 2003 - 31 March 2005.